Diffusion in Uncrosslinked Silicones

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ABSTRACT: Diffusion in poly(dimethylsiloxanes) with $M > 5 \times 10^4$ increases with increasing M, in contrast to the decrease found with lower molecular weights, and contrary to the expectation based on the statistics of polymer end groups. This is explained by an increase in free volume in the highest polymers, illustrated by a decrease in density. Translational friction coefficients vary nonlinearly with carbon number of the penetrant in contrast to the finding of Auerbach et al. Diffusion coefficients in all the silicones tested are exponentially related to carbon number except for a limited range of carbon number where diffusion decreases unusually steeply with increasing carbon number; an explanation is offered based on the orientation of the penetrant. Substitution with groups other than methyl decreases the rate of diffusion, apparently by increasing the density and thus reducing the free volume. The increase in diffusion in higher molecular weight dimethylsiloxanes has not been found in trifluoropropylmethylsiloxanes at the highest molecular weight studied.

The diffusion coefficients of organic vapors in commercial silicones, described in Table I, have been determined by the gas chromatographic method at effectively infinite dilution. The results are reported elsewhere.[1] However, a number of anomalies have appeared which are of interest to polymer chemists and these are reported here.

Hydrocarbons in Poly(dimethylsiloxane)

Diffusion coefficients at 150°C for *n*-alkanes in poly(dimethylsiloxanes) of four different molecular weights are shown in Figure 2. There are a number of interesting facets to this figure which contradict some widely held beliefs on diffusion in liquid polymers.

Effect of Polymer Molecular Weight. The four lines for the four polymer molecular weights are not coincident; the diffusion coefficients increase with increasing polymer molecular weight.

Flory's classical analysis suggests that the diffusion coefficient is independent of polymer molecular weight if this is high enough for end groups to be a negligible fraction. Tanner[2] determined diffusion coefficients of benzene in PDMS of various molecular weights and found, as expected, that they decreased with increasing molecular weight to a constant value at about $M = 5 \times 10^4$. Our results at 51° overlap Tanner's but continue to much higher molecular weights; the two sets of data are superimposed in Figure 1 and show that Tanner's lowest diffusion coefficients represent a minimum rather than an asymptote.

An increase in diffusion coefficient suggests an increase in free volume and therefore a decrease in density. This is shown in Figure 4 where literature values of the density[4–8] are plotted against polymer molecular weight. Presumably high molecular weights lead to high levels of entanglement and hence to less efficient packing structure and increased free volume.

Effect of Chain Length of *n*-Alkane Penetrant. Figure 2 shows that ln D is nearly linear with chain length of the penetrant. This is typical of the data in ref 1; the slight curvature of the line for the highest polymer and a more marked curvature at lower temperatures will be discussed in the next section.

In general, statistical analysis showed that diffusion coefficients were related to penetrant carbon number C and absolute temperature T by the equation

$$\ln D = K_0 + K_1 C + (K_2 + K_3 C)/RT \qquad (1)$$

This expression holds well for temperatures 400°K and upwards and for the lower polymers at 350°K and upwards.

Auerbach et al.[3] have found that the diffusion coefficients of homologous penetrants in natural rubber are inversely proportional to the penetrant molecular weight; this has been widely quoted in the form that the friction coefficient ζ ($\equiv kT/D$) is proportional to carbon number. Equation 1 does not reduce to this; moreover the friction coefficient is plotted against carbon number in Figure 5 and the relation is clearly not linear at any temperature.

More Complex Effect of Chain Length at Low Temperatures. While Figure 2 is typical of the data in ref 1, the plots at 50°C, the lowest temperature studied, are substantially nonlinear as shown in Figure 3. Moreover the curvature is most marked with the highest polymer. At 100°C (not shown) this pattern is less marked and at

Table I
Properties of the Silicones Used

	SE-30[c]	Viscasil[c] 100,000	SF-96-2000[c]	SF-96-200[c]	DC-550[d]	DC-710[d]	OV-25[d]	OV-210[e]	SP-2401[e]	OV-225[f]
Viscosity ctks at 25°C	9.47×10^6	100,000	2,000	200	115	475–525	>100,000	10,000	700	9,000
Av mol wt	400,000	103,000	34,975	11,000		2,600	1×10^4	2×10^5		8×10^3
Sp gr at 25°/25°C	0.966[a]	0.978	0.974	0.972	1.068	1.10	1.150	1.284	1.30	1.096
Coefficient of expansion[b] $cm^3/cm^3/°C$	9.25×10^{-4}	9.25×10^{-4}	9.25×10^{-4}	9.25×10^{-4}	4.2×10^{-4}	4.3×10^{-4}	4.3×10^{-4}	9.5×10^{-4}	9.5×10^{-4}	8.0×10^{-4}
Phenyl substitution	0	0	0	0	25	50	75	0	0	25

[a] At 29.8°C. [b] 25 to 150°C. [c] Poly(dimethylsiloxane). [d] Phenyl-substituted poly(dimethylsiloxane). [e] Poly(methyltrifluoropropyl)siloxane. [f] Poly(methylcyanopropyl(methylphenyl)siloxane).

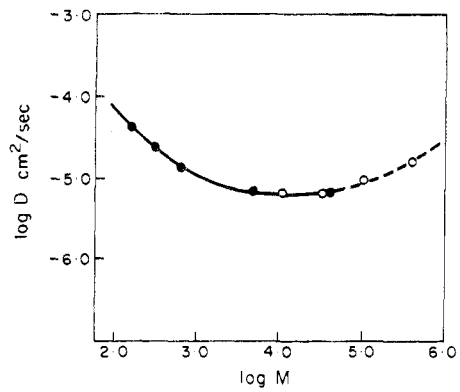

Figure 1. Diffusion of benzene in poly(dimethylsiloxane): 0–50°C in PDMS; (●) unspecified temperature in 10% benzene, 90% PDMS.

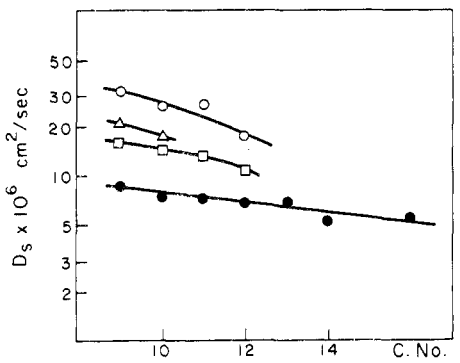

Figure 2. Variation of diffusion coefficient in PDMS with n-alkane chain length at 148 ± 3°C: ○, SE-30, $M = 4 \times 10^5$; △, Viscasil 100,000, $M = 10^5$; □, SF-96-2000, $M = 4 \times 10^4$; ●, SF-96-200, $M = 10^4$

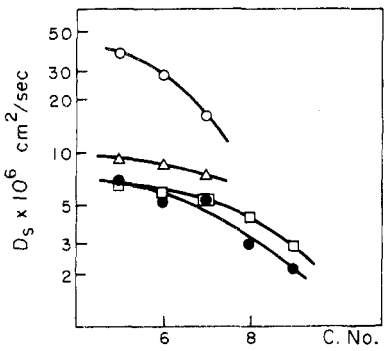

Figure 3. As Figure 2, but at 50 ± 2°C.

150°C, as shown in Figure 2, the curvature is nearly zero.

The following plausible explanation is offered. Small molecules pass between the polymer chains in any orientation, whereas long-chain molecules must pass through in needle-like formation. There is an intermediate range (about C_6 to C_9) in which there is a restricted range of orientation that can penetrate. In this intermediate range the diffusion coefficient will decline more quickly with increasing carbon number. At higher temperatures this will cease to be important because movement of the polymer segments will increase and assist the diffusion, and the free volume will also increase. The denser lower polymers have fewer large cells of free volume and so do not admit the lowest n-alkanes tested (n-pentane and upwards) in any formation other than needle-like. Our data are consistent with this explanation but do not prove it. If it is correct,

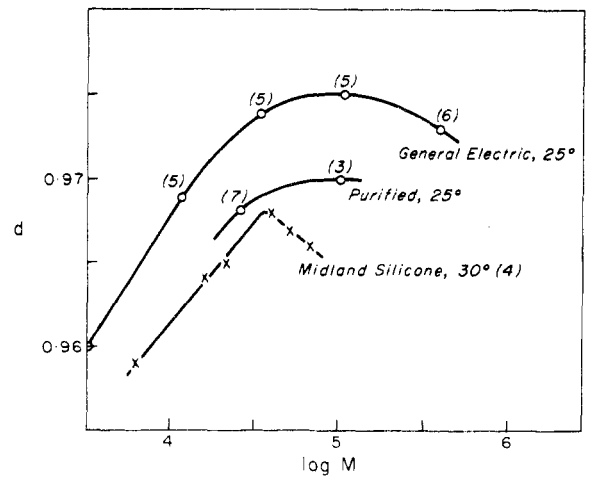

Figure 4. Variation of density of poly(dimethylsiloxane) with molecular weight.[3-6]

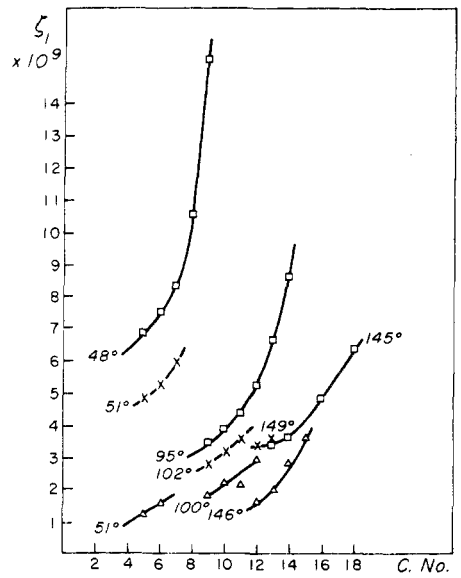

Figure 5. Translational friction coefficients of n-alkanes in poly(dimethylsiloxane): □, $M = 4 \times 10^4$; ×, $M = 1 \times 10^5$; △, $M = 4 \times 10^5$.

then there will be a range of rapid decline of diffusion coefficient in the lower polymers also, but it will be at carbon numbers below 5 or at temperatures below ambient. With the installation of better equipment here, this is being investigated.

Effect of Polymer Functional Groups

It seems to be consistently true that the diffusion coefficient decreases with polymer type in the order dimethyl > 25% phenyl > trifluoropropyl, methyl > 50% phenyl > cyanopropyl, methylphenylmethyl > 75% phenyl, as illustrated in Table II.

Statistical analysis showed that the energy of activation is linear with the polymer density and that, when this was allowed for, an increase in phenyl content decreased the temperature-independent factor of D.

In all the polymers, the data were most nearly represented by eq 1. In no case was the friction coefficient found to be linear with carbon number (see Figures 6 and 7); the nonlinearity was most marked with the trifluoropropylmethylsiloxanes.

The effect of polymer molecular weight was investigated only superficially. Two trifluoropropylmethyl silicones of

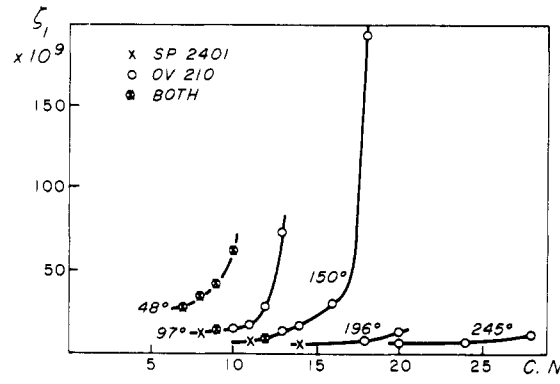

Figure 6. Translational friction coefficients of n-alkanes in trifluoropropylmethylsiloxane: ×, SP-2401, η = 700 cs; ○, OV210, η = 10,000 cs.

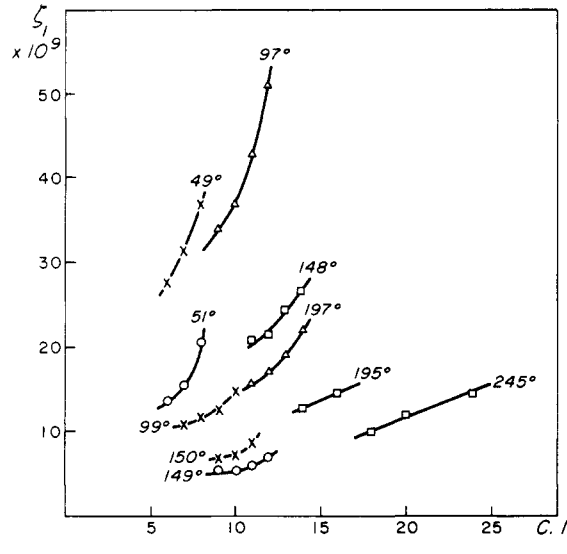

Figure 7. Translational friction coefficients of n-alkanes in phenylated silicones: ○, DC550 = 25% phenyl; △, OV225 = 25% phenyl, 25% cyanopropyl; ×, DC710 = 50% phenyl; □, OV25 = 75% phenyl.

Table II
Diffusion Coefficients of Organic Compounds in Silicones ($\times 10^7$ cm^2/sec)

	DC-550	OV-210	SP-2401	DC-710	OV-225	OV-25
m-Xylene at 98 ± 2°C	65	52	49	44	17	
n-Dodecane at 149 ± 1°C	85	66	65	60	34	27

viscosity 700 and 10,000 cs had nearly identical diffusional properties (see Figure 6). The latter had a molecular weight of 2×10^5, but this represents only 1.3×10^3 monomer units making it comparable to the PDMS with $M = 10^5$ or 1.3×10^3 monomer units. In PDMS the molecular weight effects are apparent but not well developed at $M \simeq 10^5$. A marginal molecular weight dependence might therefore be expected in the higher fluoropolymer but is not apparent, perhaps because the dipole–dipole interactions between the chains hold it more firmly into a dense structure. It will be interesting to examine a fluoropolymer of still higher molecular weight.

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References and Notes

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Communications to the Editor

Model Compounds and ^{13}C NMR Observation of Stereosequences of Polypropylene

The ^{13}C NMR spectrum of methyl carbons of stereoirregular polypropylene shows at least nine clearly distinguishable resonance peaks. These have been attributed to the pentad configurational sequences, but complete agreement on the assignment of the spectrum, especially in the region of the *mr*-centered[3] pentads, is still lacking in the literature.[4-7]

We have observed the ^{13}C NMR spectra of the 9-methyl group of 3(*S*),5(*R*),7(*RS*),9(R_aS),11(*RS*),13(*R*),15(*S*)-heptamethylheptadecane (compound A) and of a mixture of A with 3(*S*),5(*S*),7(*RS*),9(*RS*),11(*RS*),13(*R*),15(*S*)-heptamethylheptadecane (compound B).[8] The 9-methyl group of the compounds was 93% enriched in ^{13}C. The spectra are shown in Figure 1.[9]

The structures of the compounds are represented in Fischer projection in Figure 2. Actually, A and B are mixtures of several diastereoisomers. Consideration of the possible structures represented by each shows that the pentad configurational sequences around the 9-methyl of A are *mmmr*, *mmrm*, *rrmr*, and *rrrm*, while those in B are *mmmm*, *rmmr*, *mmrr*, *mrmr*, *mrrm*, and *rrrr*. Although the racemic carbons of A and B are not exactly in a 50:50 ratio owing to the method of preparation, they are nearly so; the populations of the configurational sequences in A are therefore approximately 1:1:1:1 and those in B are 1:1:2:2:1:1.

Nine chemical shifts are observed in the spectra of Figure 1, and these agree with those found, under the same conditions, in the methyl spectra of polypropylene[6] (see Table I). This observation establishes the validity of compounds A and B as models for the pentad configurational sequences in polypropylene.

A unique assignment of the pentad stereochemical shifts can be achieved by comparing the spectra of A and B (chemical shifts and relative intensities) with those of the